

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 12-6-97		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Low Temperature Reactions for the Preparation of Group 13-15 Materials from Organo-gallium(I) and -indium(I) Compounds				5. FUNDING NUMBERS Grant: N00014-96-1-0483  R&T Code: 4135002	
6. AUTHOR(S)  O.T. Beachley, Jr., Jeffrey F. Lees and Matthew J. Noble					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry State University of New York at Buffalo NSM Complex Buffalo, NY 14260-3000				8. PERFORMING ORGANIZATION REPORT NUMBER  Technical Report No. 48	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER  n/a	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited. Reproduction in whole or in part is permitted for any purpose of the United States government.				12b. DISTRIBUTION CODE  n/a	
13. ABSTRACT (Maximum 200 words) The reactions of pentamethylcyclopentadienylindium(I) $\text{In}(\text{C}_5\text{Me}_5)$ with white phosphorus ( $\text{P}_4$ ) at $175^\circ\text{C}$ and of neopentylgallium(I) $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ with $\text{P}_4$ at $350-400^\circ\text{C}$ and with $\text{NH}_3$ at $460-480^\circ\text{C}$ in sealed tubes provide routes to indium phosphide, gallium phosphide and hexagonal gallium nitride, respectively. The formation of these group 13-15 materials as black solids was confirmed by their X-ray photoelectron spectra, X-ray powder diffraction patterns and physical properties. The other products were $(\text{C}_5\text{Me}_5)_2$ in the case of the reaction of $\text{In}(\text{C}_5\text{Me}_5)$ with $\text{P}_4$ , neopentane and $\text{H}_2$ in the case of the $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n - \text{NH}_3$ reaction, and unidentified hydrocarbons and $\text{H}_2$ in the case of $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n - \text{P}_4$ . These products were isolated and identified by $^1\text{H}$ NMR spectroscopy or their physical properties, as appropriate. Carbon contamination in all materials was indicated by their XPS spectra and confirmed by combustion analysis.					
14. SUBJECT TERMS Materials, InP, GaN, GaP				15. NUMBER OF PAGES 12	
				16. PRICE CODE n/a	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		

OFFICE OF NAVAL RESEARCH

Contract N-00014-96-1-0483

R&T Code 4135002

TECHNICAL REPORT NO. 48

Low Temperature Reactions for the Preparation of Group 13-15 Materials  
from Organo-gallium(I) and -indium(I) Compounds

by

O. T. Beachley, Jr., Jeffrey F. Lees and Matthew J. Noble

State University of New York at Buffalo  
Department of Chemistry  
Buffalo, New York 14260-3000

12 June 1997

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

\*This document has been approved for public release  
and sale; its distribution is unlimited

19970625 031

# Low Temperature Reactions for the Preparation of Group 13-15 Materials from Organo-gallium(I) and -indium(I) Compounds

O. T. Beachley, Jr.,\* Jeffrey F. Lees and Matthew J. Noble

Department of Chemistry  
State University of New York at Buffalo, Buffalo, NY 14260

## ABSTRACT

The reactions of pentamethylcyclopentadienylindium(I)  $\text{In}(\text{C}_5\text{Me}_5)$  with white phosphorus ( $\text{P}_4$ ) at 175 °C and of neopentylgallium(I)  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  with  $\text{P}_4$  at 350 - 400 °C and with  $\text{NH}_3$  at 460 - 480 °C in sealed tubes provide routes to indium phosphide, gallium phosphide and hexagonal gallium nitride, respectively. The formation of these group 13-15 materials as black solids was confirmed by their X-ray photoelectron spectra, X-ray powder diffraction patterns and physical properties. The other products were  $(\text{C}_5\text{Me}_5)_2$  in the case of the reaction of  $\text{In}(\text{C}_5\text{Me}_5)$  with  $\text{P}_4$ , neopentane and  $\text{H}_2$  in the case of the  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  -  $\text{NH}_3$  reaction, and unidentified hydrocarbons and  $\text{H}_2$  in the case of  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  -  $\text{P}_4$ . These products were isolated and identified by  $^1\text{H}$  NMR spectroscopy or their physical properties, as appropriate. Carbon contamination in all materials was indicated by their XPS spectra and confirmed by combustion analysis.

Two pathways have been proposed for the formation of group 13-15 electronic materials such as GaAs and InP by using the organometallic chemical vapor deposition (OMCVD) process with the simplest precursors, a group 13 trialkyl compound and a group 15 hydride. One pathway requires a series of elimination reactions<sup>1,2</sup> with formation of species of the types,  $R_2MEH_2$  and  $RMEH$  ( $M$  = group 13 element,  $E$  = group 15 element) whereas the other involves the formation and reactions of low oxidation state species<sup>3,4</sup> such as  $MR$ ,  $E_n$  and  $EH$ . Even though many workers favor the low oxidation state pathway, very few synthetic studies have used low oxidation state compounds to prepare group 13-15 materials. However, cyclopentadienylindium(I) compounds have been reacted with  $PH_3$  at 675 °C to form InP by using a OMCVD process.<sup>5</sup> In this paper we report the results of our studies of reactions of low oxidation state organo-indium and -gallium compounds to prepare InP, and GaP and GaN, respectively. This study was prompted by our previous observations in indium(I) chemistry which had shown that pentamethylcyclopentadienylindium(I)<sup>6,7</sup> reacted readily with simple Lewis bases<sup>6</sup> such as THF and pyridine at room temperature to form indium metal and decamethylfulvene. Therefore, we investigated the reactions of  $In(C_5Me_5)$  with white phosphorus ( $P_4$ ), a nominal Lewis base with a lone pair of electrons on each phosphorus atom, in order to determine if InP could be formed at a temperature which would be significantly lower than that typically used for the OMCVD process. The success of the reaction of  $In(C_5Me_5)$  with  $P_4$  prompted additional experiments with the low oxidation state organogallium(I) compound<sup>8</sup>  $[Ga(CH_2CMe_3)]_n$  in order to learn more about the usefulness of low oxidation state compounds for the formation of materials. Thus, the reactions of  $[Ga(CH_2CMe_3)]_n$  with  $P_4$  and with  $NH_3$  in order to prepare GaP and GaN were investigated.

The reaction of  $In(C_5Me_5)$  with  $P_4$  in a simple break-seal tube in the absence of solvent at the relatively low temperature of 175 °C provides a new route to indium phosphide. Subsequent studies<sup>9</sup> have also demonstrated that the identical reagents can be

used to prepare thin films of InP under OMCVD conditions at temperatures as low as 125 °C. In the sealed tube experiments, two distinctly different products, a shiny black crystalline solid and a yellow-orange liquid which was nonvolatile at room temperature, were formed. The black product was identified, after it was washed with pentane, ground with a mortar and pestle in the dry box and then washed again with pentane, by its X-ray photoelectron spectrum<sup>10</sup> (XPS) and X-ray powder diffraction pattern<sup>11</sup> as InP. The XPS surface scan of the InP indicated the presence of In, P, C and O. With the possible



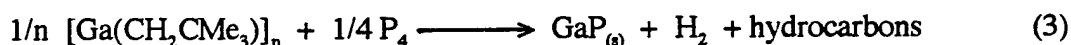
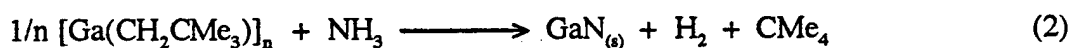
exception of phosphorus, each element was present in only one environment. The observed binding energies for indium and phosphorus are in good agreement with those previously reported for InP<sup>10</sup>. The presence of carbon in the InP was confirmed by combustion analysis (3.74%). Oxygen contamination might be related to the presence of either P<sub>4</sub>O<sub>6</sub> or P<sub>4</sub>O<sub>10</sub>, compounds which would be readily formed by a reaction of P<sub>4</sub> with oxygen (impurity) in the dry box. However, if a phosphorus oxide were present, the XPS line for phosphorus would have to be very small and lost in the noise of the spectrum. The nonvolatile, yellow-orange liquid which was separated by washing the initial reaction product with pentane was identified by <sup>1</sup>H NMR spectroscopy as (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>.<sup>6,12</sup> Even though this product can be envisioned to be formed by coupling of two C<sub>5</sub>Me<sub>5</sub> radicals, we have no data to confirm or deny the presence of radicals.

The general usefulness of the reaction of a cyclopentadienylindium(I) compound with P<sub>4</sub> was tested further by investigating the corresponding reactions of In(C<sub>5</sub>H<sub>5</sub>)<sup>13-16</sup>, In(C<sub>5</sub>H<sub>4</sub>Me)<sup>16</sup>, and In(C<sub>5</sub>H<sub>4</sub>CMe<sub>3</sub>)<sup>17</sup> by using the identical conditions as described for the In(C<sub>5</sub>Me<sub>5</sub>) reaction. A shiny black solid and a nonvolatile liquid were formed in each case. The XPS spectra of each black solid was consistent with InP. However, the black products from these reactions had carbon impurities which were higher than observed for

the  $\text{In}(\text{C}_5\text{Me}_5) - \text{P}_4$  reaction. The percent carbon in the shiny black solid (combustion analyses) increased in the order  $\text{In}(\text{C}_5\text{Me}_5)$  (3.74 %)  $\ll$   $\text{In}(\text{C}_5\text{H}_4\text{CMe}_3)$  (15.95 %)  $<$   $\text{In}(\text{C}_5\text{H}_4\text{Me})$  (21.77 %)  $<$   $\text{In}(\text{C}_5\text{H}_5)$  (26.18%). The liquid products isolated from the reactions of these cyclopentadienylindium(I) compounds had complicated  $^1\text{H}$  NMR spectra. Even though these organic products were not conclusively identified, they can be envisioned to be compounds related to  $(\text{C}_5\text{Me}_5)_2$  which had either polymerized and/or decomposed as would be consistent with the chemistry of a cyclopentadiene derivative. The order for the carbon contamination suggests that it might be related to the ease of decomposition of the organic product and the reaction conditions. A reaction in a sealed tubes eliminates the possibility of removing the organic product as it is formed.

Although all four indium(I) reagents produced approximately the same results, the reaction between  $\text{In}(\text{C}_5\text{Me}_5)$  and  $\text{P}_4$  provided some significant observations that suggest that it might be the best reagent to use to prepare  $\text{InP}$ . First, the reaction between  $\text{In}(\text{C}_5\text{Me}_5)$  and  $\text{P}_4$  appears to occur, at least in part, in the gas phase. Even though the starting materials were placed in the bottom of the break-seal tube and liquified at the reaction temperature of  $175^\circ\text{C}$ , the entire surface of the glass tube became mirrored with the shiny black film of  $\text{InP}$ . In contrast, the reactions of the other indium(I) derivatives produced shiny black solids where the original reagents had liquified rather than films on the entire glass surfaces of the tubes. Second, the organic product from the  $\text{In}(\text{C}_5\text{Me}_5)$  and  $\text{P}_4$  reaction was readily removed from the indium phosphide with one pentane wash to leave a very fine powder. The XPS spectrum of the black solid had a very smooth base line from which it was easy to detect the lines for the contaminants as well as the Auger peaks for indium and phosphorus. The X-ray powder pattern confirmed the black shiny solid to be  $\text{InP}$ .<sup>11</sup> However, the powder pattern also revealed the presence of indium metal.<sup>18</sup> It is noteworthy that the XPS spectrum did not suggest indium in two different environments. Either the XPS spectrometer could not resolve a peak for  $\text{InP}$  at 444.2 eV and for indium metal at 443.1 eV or the amount of indium metal was too small to detect.

The low oxidation state organogallium(I) compound<sup>8</sup>  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  has been used to prepare hexagonal gallium nitride and gallium phosphide but at higher temperatures than those used for the reactions of the cyclopentadienyindium(I) compounds. The reaction with  $\text{NH}_3$  at 460 - 480 °C (heating for 1 d) and the reaction with  $\text{P}_4$  at the slightly lower temperature of 350 - 400 °C (heating for 8 d) can be summarized by the following chemical equations (eq 2 and 3). Both shiny black solids were crystalline and were identified by their X-ray photoelectron spectra<sup>10, 19,20</sup> and X-ray powder diffraction patterns.<sup>21</sup>



The binding energies observed from XPS spectra identified Ga, N, C and O for the sample believed to be gallium nitride and Ga, P, C and O for the gallium phosphide. The presence of carbon was confirmed by combustion analyses. The gallium nitride had a lower carbon impurity (1.24 % C) than did the gallium phosphide (9.97 % C). The amount of oxygen in the samples as detected by XPS was small. In the case of the reaction of  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  with  $\text{NH}_3$ , the volatile products were isolated by using the vacuum line and identified as only  $\text{H}_2$  and neopentane ( $\text{CMe}_4$ ). The percent yields of  $\text{H}_2$  and  $\text{CMe}_4$ , as based on eq 2, were 70.3 and 86.6, respectively. The neopentane was identified by  $^1\text{H}$  NMR spectroscopy as the only hydrocarbon product. In the case of the reaction of  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  with  $\text{P}_4$ , the  $^1\text{H}$  NMR spectrum suggested the volatile product to be a mixture of hydrocarbons.

The experimental results from this study support the hypothesis that low oxidation state species might be important to the formation of group 13 - 15 materials. Cyclopentadienyindium(I) compounds react with  $\text{P}_4$  at a relatively low temperature. Even though a similar low temperature could not initiate the corresponding reaction of  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ , the surprisingly clean and straightforward reaction of this gallium(I)

compound with ammonia at a temperature lower than is typical for trialkylgallium(III) - ammonia reactions (600 - 1000 °C)<sup>22</sup> is significant. The differences between the temperatures needed for reactions of the gallium(I) and indium(I) compounds might reflect major differences between these two types of reagents. Cyclopentadienylindium(I) compounds have very weak intermolecular interactions between the simplest formula units in the solid state, are volatile at room temperature<sup>6,7,13-17</sup> and are monomeric in the gas phase.<sup>6,16</sup> In contrast,  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ , is nonvolatile at room temperature and is believed to exist as clusters<sup>8</sup> of gallium atoms with gallium-gallium bonding. Cryoscopic molecular weight studies for benzene solutions suggest that the clusters might have from six to twelve gallium atoms. Thus, the higher temperature needed for reactions of gallium(I) than for indium(I) might be related to the existence of these gallium-gallium bonds. The significance of the low oxidation state gallium reactant can be appreciated when the experimental observations for the reaction of  $\text{P}_4$  with a gallium(III) reagent  $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$  and with the gallium(I) compound  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  under the same conditions are compared. When  $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$  was reacted with  $\text{P}_4$  at 350 - 400 °C, the black solid product was composed of GaP and gallium metal, had higher carbon contamination (12.11 %) than when the gallium(I) reagent was used, and had broad XRD lines. Silver-colored specks of gallium metal which were observed by microscopic examination melted at 31 - 37 °C. The melting point of pure gallium metal is 29.8 °C.

## EXPERIMENTAL

Cyclopentadienylindium(I) compounds,  $\text{In}(\text{C}_5\text{H}_5)^{16}$ ,  $\text{In}(\text{C}_5\text{H}_4\text{Me})^{16}$ ,  $\text{In}(\text{C}_5\text{H}_4\text{CMe}_3)^{17}$ , and  $\text{In}(\text{C}_5\text{Me}_5)^{6,7}$ , and neopentylgallium(I)<sup>8</sup>  $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$  were prepared and purified by the literature methods. These compounds are exceedingly sensitive to oxygen and moisture and must be manipulated in either a standard vacuum line or in a purified argon atmosphere by using the procedures described previously.<sup>6,7</sup> White phosphorus under water was purchased from Strem Chemicals, Inc.. Small chunks of the

white phosphorus were cut from the larger piece and placed in a small flask. Water was then removed by vacuum distillation. The smaller pieces used for the reactions were cut from the larger pieces in the dry box. Ammonia was dried over sodium metal before use. All manipulations of the shiny black products, InP, GaP and GaN, were carried out in the drybox. Elemental analyses for carbon were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The  $^1\text{H}$  NMR spectra were recorded by using a Varian Gemini 300 FT-NMR spectrometer operating at 300 MHz. Chemical shifts are reported in  $\delta$  units (ppm) and are referenced to  $\text{SiMe}_4$  at 0.00 and  $\text{C}_6\text{H}_6$  at 7.15. Each sample for XPS analysis was first ground into a fine powder in the dry box and then the sample was placed on one side of two-sided clear sticky tape which was fixed to the circular metal mounting stage. The mounting stage was then placed in the XPS manipulator chamber in the dry box in order to transfer the sample to the spectrometer without exposure to air. The XPS analysis was performed by using a Perkin-Elmer Physical Electronics (PHI) Model 5100 ESCA spectrometer with a  $\text{Mg K}_{\alpha 1,2}$  X-ray source (1253.6 eV) with a  $180^\circ$  hemispherical detector. The spectrometer was calibrated to the  $\text{Ag } 3d_{5/2}$  peak at 367.9 eV with full width at half maximum of 900,000 counts per second. The linearity of the binding scale was calibrated by using  $\text{Cu } 2p_{3/2}$  and  $\text{Cu } 3p_{3/2}$  at 932.5 and 75.0 eV, respectively. The operating parameters of the X-ray source were 300 W, 15kV, and 20 mA. The base pressure of the instrument was  $2 \times 10^{-9}$  Torr with an operating pressure of  $2 \times 10^{-8}$  Torr. The spectra were collected with a take-off angle of  $45^\circ$ . The identity of the different elements present at the surface of the sample were qualitatively evaluated by low resolution (89.45 eV) survey spectra. High resolution (35.75 eV) spectra were taken to establish the binding energy. X-ray powder diffraction patterns were obtained by using a Siemens D-500 X-Ray Diffractometer. The powder sample was irradiated with monochromatic  $\text{Cu K}_\alpha$  radiation at a wavelength of  $1.54 \text{ \AA}$ . Power settings were 30 mA and 40 kV. The powder pattern was generated as  $2\theta$  versus intensity. The peak locations were translated into d spacings and then compared to ASTM standards.

**Reaction of  $\text{In}(\text{C}_5\text{Me}_5)$  with  $\text{P}_4$ .** A break-seal tube was charged with 1.71 g of  $\text{In}(\text{C}_5\text{Me}_5)$  (6.45 mmol) and 0.209 g of  $\text{P}_4$  (1.68 mmol), was evacuated with the tube at  $-196^\circ\text{C}$  and then was sealed by fusion. The tube was placed in an oven at  $175^\circ\text{C}$ . Since  $\text{P}_4$  melts at  $\sim 41^\circ\text{C}$  and  $\text{In}(\text{C}_5\text{Me}_5)$  melts at  $\sim 92^\circ\text{C}$ , the contents became liquid in a matter of minutes and turned black. After approximately 15 min, the entire internal surface of the tube was coated with a black film. The tube was heated for a total of 3 d in order to ensure complete reaction. The seal was broken, the tube was evacuated and the solid was washed with pentane to separate a yellow-orange pentane soluble liquid from the black solid. The solid was scraped from the tube and weighed (0.766 g, 5.25 mmol  $\text{InP}$ , 81.4 % yield based on  $\text{In}(\text{C}_5\text{Me}_5)$ ). The  $^1\text{H}$  NMR spectrum of the yellow-orange liquid was comparable to the spectrum previously observed for decamethylfulvene but additional lines were also evident.  **$\text{InP}$  ESCA** (Binding energy, eV; corrected to  $\text{C}_{1s}$ ): 444.7 ( $\text{In}_{d5/2}$ ); 452.3 ( $\text{In}_{d3/2}$ ); 129.2 ( $\text{P}_{2p}$ ); 285.0 ( $\text{C}_{1s}$ ); 532.6 ( $\text{O}_{2p}$ ) (Lit.<sup>10</sup>  $\text{In}_{d5/2}$  444.2;  $\text{P}_{2p}$  129.0;  $\text{C}_{1s}$  285.0;  $\text{O}_{2p}$  531.9). X-ray Powder Pattern (d spacings): 3.36 ( $\text{InP}$ ); 2.70 ( $\text{In}$ ) (Lit.  $\text{InP}$  3.39<sup>11</sup>;  $\text{In}$  2.72<sup>18</sup>). Anal. Found: C, 3.74.

**Reaction of Other Cyclopentadienylindium(I) Derivatives with  $\text{P}_4$ .** All other reactions of cyclopentadienylindium(I) compounds with  $\text{P}_4$  were run in a manner similar to that described previously for  $\text{In}(\text{C}_5\text{Me}_5)$ . Thus, only quantities of reagents and of  $\text{InP}$  which were isolated after it was transferred from the reaction tube and washed with pentane as well as significant experimental observations are described.  **$\text{In}[\text{C}_5\text{H}_4(\text{CMe}_3)]$ :** 0.407 g (1.73 mmol)  $\text{In}[\text{C}_5\text{H}_4(\text{CMe}_3)]$ , 0.0560 g (0.452 mmol)  $\text{P}_4$ , 0.193 g of the black solid ( $\text{InP}$ ). The reaction appeared to occur in the liquid phase as the product was located at the bottom of the tube where the reagents mixed. ESCA (Binding energy, eV; corrected to  $\text{C}_{1s}$ ): 444.5 ( $\text{In}_{d5/2}$ ); 452.2 ( $\text{In}_{d3/2}$ ); 129.3 ( $\text{P}_{2p}$ ); 285.0 ( $\text{C}_{1s}$ ); 532.6 ( $\text{O}_{2p}$ ). Anal. Found: C, 15.95.  **$\text{In}[\text{C}_5\text{H}_4(\text{Me})]$ :** 0.248 g (1.28 mmol)  $\text{In}[\text{C}_5\text{H}_4(\text{Me})]$ , 0.0386 g (0.313 mmol)  $\text{P}_4$ , 0.194 g of the black solid ( $\text{InP}$ ). The reaction appeared to occur as soon as the reagents were in the liquid phase; the product was located at the bottom of the tube where the

reagents initially mixed. ESCA (Binding energy, eV; corrected to  $C_{1s}$ ): 445.1 ( $In_{d5/2}$ ); 452.5 ( $In_{d3/2}$ ); 130.2 ( $P_{2p}$ ); 285.0 ( $C_{1s}$ ); 532.9 ( $O_{2p}$ ). Anal. Found: C, 21.77.  $In(C_5H_5)$ : 0.430 g (2.39 mmol)  $In(C_5H_5)$ , 0.0740 g (0.610 mmol)  $P_4$ , 0.253 g of the black solid ( $InP$ ). The reaction appeared to occur as soon as the reagents were in the liquid phase; the product was located at the bottom of the tube where the reagents initially mixed. ESCA (Binding energy, eV; corrected to  $C_{1s}$ ): 445.1 ( $In_{d5/2}$ ); 452.6 ( $In_{d3/2}$ ); 129.9 ( $P_{2p}$ ); 285.0 ( $C_{1s}$ ); 532.2 ( $O_{2p}$ ). Anal. Found: C, 26.18.

**Reaction of  $[Ga(CH_2CMe_3)]_n$  with  $NH_3$ .** A break-seal tube was charged with 0.440 g of  $Ga(CH_2CMe_3)$  (3.13 mmol) and 3.44 mmol of  $NH_3$ , sealed and heated at 460 - 480 °C for 24 h. As heating occurred, the contents of the tube changed color from dark reddish-brown, to light grey, to yellow-grey, and finally to black. After the tube was cooled to -196 °C, the noncondensable gas was measured with a Toepler pump - gas buret assembly (2.20 mmol  $H_2$ , 70.3% based on  $Ga(CH_2CMe_3)$  and eq 3). The volatile, condensable materials were removed from the reaction tube by vacuum distillation and identified by  $^1H$  NMR spectroscopy as neopentane,  $CMe_4$  (0.195 g, 2.71 mmol, 86.6 % based on  $Ga(CH_2CMe_3)$  and eq 3). The nonvolatile, shiny black solid was isolated and identified as  $GaN$  (0.232 g, 2.77 mmol, if entirely  $GaN$ , 88.5 % based on  $Ga(CH_2CMe_3)$  and eq 3).  **$GaN$ :** ESCA (Binding energy, eV; corrected to  $C_{1s}$ ): 20.3 ( $Ga_{3d3/2}$ ); 1119.5 ( $Ga_{2p3/2}$ ); 398.3 ( $N_{1s}$ ); 285.0 ( $C_{1s}$ ); 531.7 ( $O_{1s}$ ) (Lit.<sup>10, 19, 20</sup> 19.8 ( $Ga_{3d3/2}$ ); 1124.1 ( $Ga_{2p3/2}$ ); 397.0 ( $N_{1s}$ ); 285.0 ( $C_{1s}$ ); 531.9 ( $O_{1s}$ )). X-ray Powder Pattern: high quality, crystalline sample, hexagonal  $GaN$  structure; d spacings: 2.76, 2.58, 2.44, 1.89, 1.60, 1.46, 1.37 (Lit.<sup>21</sup> 2.76, 2.59, 2.43, 1.88, 1.59, 1.46 1.38). Anal. Found: C, 1.24; H, 0.69.

**Reaction of  $[Ga(CH_2CMe_3)]_n$  with  $P_4$ .** A break-seal tube was charged with 0.461 g of  $Ga(CH_2CMe_3)$  (3.27 mmol) and 0.102 g of white phosphorus  $P_4$  (0.820 mmol) and then heated at 350 - 400 °C for 8 d. As reaction occurred, the tube became coated (appeared like a mirror) while the material at the bottom of the tube changed from the

dark reddish-brown color of the gallium(I) reagent to shiny black. The tube was cooled to  $-196\text{ }^{\circ}\text{C}$ , opened and the noncondensable gas ( $\text{H}_2$ ) (1.41 mmol) was measured with a Toepler pump-gas buret assembly. The remaining materials which were volatile at room temperature were vacuum distilled into a small tube, weighed (0.115 g) and characterized by  $^1\text{H}$  NMR spectroscopy. The nonvolatile, shiny black solid was scraped from the tube, ground into a fine powder, washed with 50 mL pentane and weighed in the drybox (0.343 g, 3.40 mmol, if entirely GaP, 104 % yield based on  $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ ). **GaP**: ESCA (Binding energy, eV; corrected to  $\text{C}_{1s}$ ): 19.6 ( $\text{Ga}_{3d_{3/2}}$ ); 1118.8 ( $\text{Ga}_{2p_{3/2}}$ ); 129.5 ( $\text{P}_{2p}$ ); 285.0 ( $\text{C}_{1s}$ ); 532.9 ( $\text{O}_{1s}$ ) (Lit.<sup>10, 19, 20</sup> 19.8 ( $\text{Ga}_{3d_{3/2}}$ ); 1124.1 ( $\text{Ga}_{2p_{3/2}}$ ); 128.8 ( $\text{P}_{2p}$ ); 285.0 ( $\text{C}_{1s}$ ); 531.9 ( $\text{O}_{1s}$ )). X-ray Powder Pattern: high crystalline quality; d spacings: 3.14, 2.72, 1.93, 1.65, 1.26, 1.23 (Lit.<sup>21</sup> 3.15, 2.73, 1.93, 1.25, 1.22). Anal. Found: C, 9.97; H, 0.94.

**Reaction of  $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$  with  $\text{P}_4$ .** A break-seal tube was charged with 0.887 g of  $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$  (3.13 mmol) and 0.0998 g of  $\text{P}_4$  (0.805 mmol), sealed and heated at  $350 - 400\text{ }^{\circ}\text{C}$  for 24 h. As heating occurred, the tube became coated with a light brown mirror-like coating while a shiny black material formed in the bottom of the tube. After the tube was cooled to  $-196\text{ }^{\circ}\text{C}$ , the noncondensable gas was measured with a Toepler pump - gas buret assembly (2.92 mmol  $\text{H}_2$ ). The volatile materials (0.482 g) were removed by vacuum distillation and characterized by  $^1\text{H}$  NMR spectroscopy. The presence of numerous lines between 0.00 and 5.00 ppm ( $\text{C}_6\text{D}_6$ ) suggested the sample to be a mixture of unidentifiable hydrocarbons. The nonvolatile, shiny black solid was scraped out of the reaction tube in the drybox, washed with 50 mL of pentane and weighed (0.302 g). This material appeared as a shiny black solid to the naked eye but microscopic examination revealed a mixture of a shiny black solid with silver-colored specks. Characterization data identified a mixture of GaP and gallium metal. Mp: Silver-colored specks melted at  $31 - 37\text{ }^{\circ}\text{C}$ , but the black solid did not melt up to  $260\text{ }^{\circ}\text{C}$ . ESCA (Binding energy, eV; corrected to  $\text{C}_{1s}$ ): 20.0 ( $\text{Ga}_{3d_{3/2}}$ ); 1119.3 ( $\text{Ga}_{2p_{3/2}}$ ); 130.3 ( $\text{P}_{2p}$ ); 285.0 ( $\text{C}_{1s}$ ); 532.9 ( $\text{O}_{1s}$ ). X-ray Powder

Pattern: broad lines, poor crystalline quality; d spacings: 3.12, 1.92 1.64, 1.25, 1.22.

Anal. Found: C, 12.11; H, 1.64.

**Acknowledgements.** This work was supported in part by the Office of Naval Research. The authors thank Dr. Patricia Costanzo, Department of Geology, University at Buffalo for her help to obtain the X-ray powder diffraction data and Norma deGatica, Department of Chemistry, University at Buffalo for her help with the XPS spectra.

### References

1. Schyler, D.: Ring, M. A. *J. Organomet. Chem.* **1976**, *114*, 9.
2. Schyler, D.: Ring, M. A. *J. Electrochem. Soc.* **1977**, *124*, 569.
3. Reep, D. H.; Ghandi, S. K. *J. Electrochem. Soc.* **1983**, *130*, 675.
4. Haigh, J. ; O'Brien, S. *J. Cryst. Growth* **1984**, *68*, 550.
5. Staring, E. G. J.; Meekes, G. J. M. *J. Am. Chem. Soc.* **1989**, *111*, 7648.
6. Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettingner, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346.
7. Beachley, O. T., Jr.; Churchill, M. R.; Fettingner, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666.
8. Beachley, O. T., Jr.; Pazik, J. C.; Noble, M. J. *Organometallics* **1994**, *13*, 2885.
9. McCombe, B. D.; Jiang, H. Department of Physics, State University of New York at Buffalo, Unpublished observations.
10. Gann, R. G.; Geib, K. M.; Wilmsen, C. W.; Costello, J.; Hrychowain, G.; Zeto, R. *J. J. Appl. Phys.* **1988**, *63*, 506.
11. Addamiano, A. J. *J. Am. Chem. Soc.* **1960**, *82*, 1537.
12. (a) Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141. (b) Macomber, D. W.;

- Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325.
13. Fischer, E. O.; Hofmann, H. P. *Angew. Chem.* **1957**, *69*, 639.
14. Poland, J. S.; Tuck, D. G. *J. Organomet. Chem.* **1972**, *42*, 307.
15. Peppe, C.; Tuck, D. G.; Victoriano, L. *J. Chem. Soc., Dalton Trans.* **1981**, 2592.
16. Beachley, O. T., Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fetting, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051.
17. Beachley, O. T., Jr.; Lees, J. F.; Rogers, R. D. *J. Organomet. Chem.* **1991**, *418*, 165.
18. Swanson, C.; Fuyat, D. NBS Circular; NBS: Washington, DC, **1953**, Vol. 3, p. 539.
19. Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, S. F. *Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Physical Electronics: Eden Prairie, MN, **1979**.
20. Murty, P. S.; Bhaskara Rao, S. V. N.; Sharma, S. K.; Grampurohit, S. V. *Current Sci.* **1982**, *51*, 468.
21. *JCPDS Powder Diffraction File Search Manual*; International Center for Diffraction Data: Swarthmore, PA.
22. Addamiano, A. *J. Electrochem. Soc.* **1961**, *108*, 1072. Munir, Z. A.; Searcy, A. W. *J. Chem. Phys.* **1965**, *42*, 4223. Pichugin, I. G.; Searcy, D. A. *Inorg. Mater.* **1970**, *6*, 1732. Isherwood, B. J.; Wickenden, D. K. *J. Mater. Sci.* **1970**, *5*, 869. Ejder, E.; *J. Cryst. Growth* **1974**, *22*, 44. Ogino, T.; Aoki, M. *Jpn. J. Appl. Phys.* **1979**, *18*, 1049.

**TECHNICAL REPORT DISTRIBUTION LIST - GENERAL**

Office of Naval Research (1)\*  
Chemistry Division, ONR 331  
800 North Quincy Street  
Arlington, Virginia 22217-5660

Dr. Richard W. Drisko (1)  
Naval Facilities & Engineering  
Service Center  
Code L52  
Port Hueneme, CA 93043

Defense Technical Information  
Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314

Dr. Eugene C. Fischer (1)  
Code 2840  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, D.C. 20375-5320

Dr. John Fischer, Director (1)  
Chemistry Division, C0235  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Peter Seligman (1)  
Naval Command, Control and  
Ocean Surveillance Center  
RDT&E Division  
San Diego, CA 92152-5000

\* Number of copies to forward